



TITLE:

<International Research Center for Elements Science>Organometallic Chemistry

AUTHOR(S):

CITATION:

<International Research Center for Elements Science>Organometallic Chemistry. ICR Annual Report 2016, 23: 54-55

ISSUE DATE:

2016

URL:

<http://hdl.handle.net/2433/219043>

RIGHT:

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International Research Center for Elements Science – Organometallic Chemistry –

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Scope of Research

This laboratory aims to establish new synthetic methodologies and new functional materials by designing well-defined catalysts based on transition metal chemistry. New concepts and ideas of molecular-based catalysts are accumulated by mechanistic investigations using experimental methods such as spectroscopy and kinetic techniques, as well as theoretical methods. The research subjects include: 1) development of novel organotransition metal systems for catalysis based on precise ligand design, and 2) preparation of π -conjugated polymers using direct arylation.

KEYWORDS

Transition Metal Complex
Homogeneous Catalyst
Reaction Mechanism
Low-coordinate Phosphorus Ligand
 π -Conjugated Polymer



Selected Publications

Takeuchi, K.; Taguchi, H.; Tanigawa, I.; Tsujimoto, S.; Matsuo, T.; Tanaka, H.; Yoshizawa, K.; Ozawa, F., A Square Planar Complex of Platinum(0), *Angew. Chem. Int. Ed.*, **55**, 15347-15350 (2016).

Ozawa, F.; Nakajima, Y., PNP-Pincer Type Phosphaalkene Complexes of Late Transition Metals, *Chem. Rec.*, **16**, 2314-2323 (2016).

Taguchi, H.; Sasaki, D.; Takeuchi, K.; Tsujimoto, S.; Matsuo, T.; Tanaka, H.; Yoshizawa, K.; Ozawa, F., Unsymmetrical PNP-Pincer Type Phosphaalkene Ligands Protected by a Fused-Ring Bulky Eind Group: Synthesis and Applications to Rh(I) and Ir(I) Complexes, *Organometallics*, **35**, 1526-1533 (2016).

Iizuka, E.; Wakioka, M.; Ozawa, F., Mixed-Ligand Approach to Palladium-Catalyzed Direct Arylation Polymerization: Effective Prevention of Structural Defects Using Diamines, *Macromolecules*, **49**, 3310-3317 (2016).

Nakajima, Y.; Tsujimoto, T.; Chang, Y.-H.; Takeuchi, K.; Ozawa, F., Reactions of [Cu(X)(BPEP-Ph)] (X = PF₆, SbF₆) with Silyl Compounds. Cooperative Bond Activation Involving Non-coordinating Anions, *Dalton Trans.*, **45**, 2079-2084 (2016).

A Square Planar Complex of Platinum(0)

The Pt(0) complex [Pt(PPh₃)(Eind₂-BPEP)] with a pyridine-based PNP-pincer-type phosphalkene ligand (Eind₂-BPEP) has a highly planar geometry around Pt with $\Sigma(\text{Pt}) = 358.6^\circ$. This coordination geometry is very uncommon for formal d¹⁰ complexes, and the Pd and Ni homologues with the same ligands adopt distorted tetrahedral geometries. DFT calculations reveal that both the Pt and Pd complexes are M(0) species with nearly ten valence electrons on the metals whereas their atomic orbital occupancies are evidently different from one another. The Pt complex has a higher occupancy of the atomic 6s orbital because of strong s–d hybridization due to relativistic effects, thereby adopting a highly planar geometry reflecting the shape and orientation of the partially unoccupied d_{x²–y²} orbital.

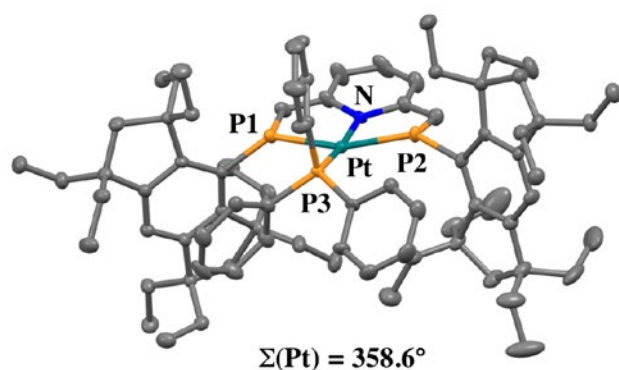


Figure 1. Molecular Structure of [Pt(PPh₃)(Eind₂-BPEP)].

Unsymmetrical PNP-Pincer Type Phosphaalkene Ligands Protected by a Fused-Ring Bulky Eind Group: Synthesis and Applications to Rh(I) and Ir(I) Complexes

Unsymmetrical PNP-pincer type phosphalkene ligand 2-(Phospholanylmethyl)-6-(2-phosphaethenyl)pyridine (Eind-PPEP) protected by an octaethyl-s-hydrindacen-4-yl (Eind) group was synthesized. The fused-ring bulky Eind

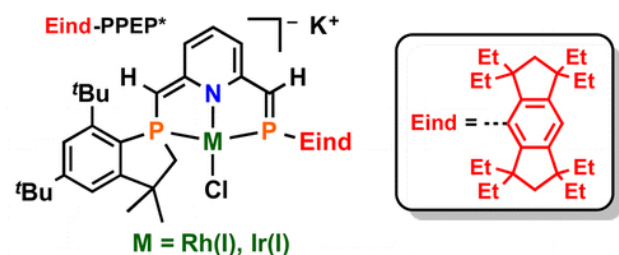
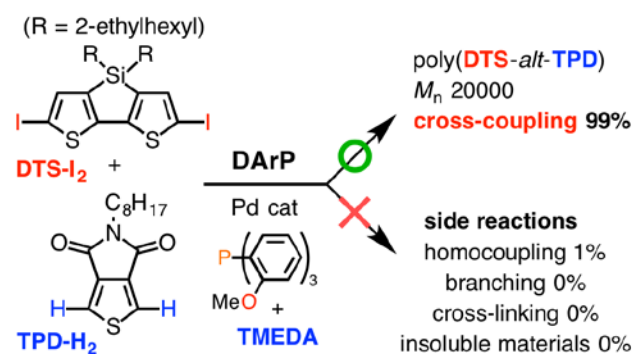


Figure 2. Non-innocent PNP-pincer type phosphalkene ligand protected by a fused-bulky Eind group.

group successfully prevents the loss of the P=C bond and enables us to compare the reactivity of Rh(I) and Ir(I) complexes toward ammonia. The complex K[RhCl(Eind-PPEP*)], bearing a dearomatized Eind-PPEP* ligand, undergoes simple ligand displacement to give [Rh(NH₃)(Eind-PPEP*)], whereas the iridium analogue K[IrCl(Eind-PPEP*)] causes N–H bond cleavage to form [Ir(NH₂)(Eind-PPEP*)]. DFT calculations indicate a thermodynamic cause of the metal-dependent product change.

Mixed-Ligand Approach to Palladium-Catalyzed Direct Arylation Polymerization: Effective Prevention of Structural Defects Using Diamines

We found a novel mixed ligand catalyst for palladium-catalyzed direct arylation polymerization (DARp) of 2,6-diiododithienosilole (DTS-I₂) and thienopyrroledione (TPD-H₂) to give poly(DTS-*alt*-TPD). It has been documented that this monomer combination has a marked tendency to form homocoupling and branching defects in polymer chains, and the latter defects eventually lead to the formation of insoluble materials. In this study, we demonstrated that the combined use of P(*o*-MeOC₆H₄)₃ and TMEDA ligands effectively prevents the defect formation. The side reactions that afford structural defects constitute a sequential process triggered by the reduction of DTS-I units. TMEDA as a simple diamine effectively inhibits the reduction of DTS-I units, giving poly(DTS-*alt*-TPD) ($M_n^{\text{GPC}} = 20,000$) in high cross-coupling selectivity (99%).



Scheme 1.